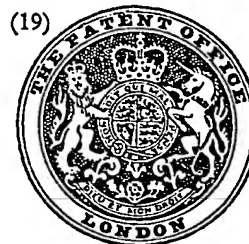


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(54) PURIFICATION AND RECOVERY OF PHENOLS

(71) We, UNION CARBIDE CORPORATION, a corporation organised and existing under the laws of the state of New York, United States of America, of 270 Park Avenue, New York, State of New York 10017, United States of America, (assignee of FREDERIC MILLER KONRAD and JOACHIM EMIL FREUDEWALD), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the purification and recovery of a phenol from a substantially anhydrous mixture containing a phenol and carbonyl-containing impurities, as for example result from the cleavage of a hydroperoxide produced by the oxidation of an alkyl substituted, aromatic hydrocarbon, such as cumene and secondary-butylbenzene, by contacting the mixture with an acidic, ion-exchange resin and thereafter subjecting the mixture to a distillation operation with the result that a purified phenol is recovered as the distillate.

The production of a phenol, on a commercial scale, can be conveniently carried out by oxidizing an alkyl substituted, aromatic hydrocarbon, such as cumene or secondary-butylbenzene, to the corresponding hydroperoxide and cleaving the hydroperoxide, usually by the use of an acid catalyst, to form a mixture containing a phenol, an aliphatic ketone, unreacted starting materials and carbonyl-containing impurities. The precise aliphatic ketone produced will depend upon the initial starting material. As an illustration, when cumene is the starting material, the aliphatic ketone produced is acetone; and when secondary-butylbenzene is the starting material, the aliphatic ketone produced is methyl ethyl ketone. The mixture is then neutralized and thereafter fractionally distilled to separate the phenol product from the other constituents of the mixture.

It has been found, however, that even with highly efficient fractionating columns, the

phenol product recovered contains small but detrimental amounts of carbonyl-containing impurities. These impurities are formed during the oxidation, cleavage and phenol product separation steps and are primarily carbonyl-containing impurities e.g. mesityl oxide.

Carbonyl-containing impurities are especially troublesome as they cannot be separated from a phenol by a simple distillation operation. Also, carbonyl-containing impurities are especially detrimental as they tend to react with the phenol, during subsequent use of the phenol in the production of such commercially important bisphenols as 2,2 - bis(4 - hydroxyphenyl)propane, to form products which impart an undesirable color to the bisphenols.

The bisphenol, 2,2 - bis(4 - hydroxyphenyl)propane, commonly referred to as Bisphenol-A, is generally produced by reacting phenol with acetone in an acidic reaction medium. It is during this reaction that the carbonyl-containing impurities react with phenol to produce products which impart an undesirable color to the Bisphenol-A. Consequently, discolored Bisphenol-A is unacceptable for use in the preparation of clear polymers such as polycarbonates which have been widely used as a substitute for glass in the preparation of window panes.

Removal of undesirable carbonyl-containing impurities from a phenol resulting from the cleavage of a hydroperoxide, as previously described, has been attempted by various diverse means. As an illustration, it has been proposed to add about five percent by weight water to the phenol, so produced, described in detail in British patent 1,108,584 and to heat the resultant mixture at elevated temperatures, generally about 95°C., while maintaining the mixture in contact with an acidic ion-exchange resin. It is alleged that heating the water-phenol mixture at elevated temperatures, while the mixture is in contact with an ion-exchange resin, will result in a conversion of the carbonyl-containing impurities to compounds having boiling points lower than the boiling point of the phenol. Consequently, it is further alleged that the "converted"

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impurities, having boiling points lower than the boiling point of the phenol, can be separated as distillates from the phenol by a simple distillation operation.

5 In actuality, however, the addition of five percent by weight water and the subsequent treatment of the water-phenol mixture, as described in the preceding paragraph, has not proved to be an efficient and/or effective process for the purification and recovery of phenol. Phenol co-distills with the water, with attendant loss of recovery efficiency, with the result that during the distillation operation, the phenol-water mixture distills over the low-boiling impurities.

10 The present invention eliminates the formation of the undesirable water-phenol distillate with all of the attendant disadvantages, inherent in the process wherein water is used in the manner previously described.

20 This invention provides for the purification and recovery of a phenol in a simple and efficient operation by which the purified phenol recovered can be used to produce such commercially important products as high quality Bisphenol-A suitable for use in the production of clear, aesthetically attractive polymers such as polycarbonates, poly(hydroxyethers), polysulfones and the like.

30 According to the present invention there is provided a process for the purification and recovery of a phenol from a substantially anhydrous mixture, containing said phenol and carbonyl-containing impurities which comprises contacting said mixture with a solid acidic ion-exchange resin which is insoluble in said mixture and which has pendant acid groups chemically bonded thereto to convert carbonyl-containing impurities to products having boiling points higher than the boiling point of said phenol and distilling the phenol therefrom.

40 A suitable anhydrous mixture for treatment in accordance with the present invention results from the cleavage of a hydroperoxide produced by the oxidation of an alkyl substituted aromatic hydrocarbon.

45 The term "substantially anhydrous" as used throughout this specification, with respect to the mixture containing phenol and carbonyl-containing impurities, means a mixture containing a maximum of 2.5 percent by weight water, when in contact with and in equilibrium with the ion-exchange resin. A condition of equilibrium exists when there is no water-exchange between the ion-exchange resin and the phenol.

55 Ion-exchange resins which are suitable for purposes of this invention are solid, insoluble resins (insoluble in the phenol-carbonyl-containing impurity mixture) made up of polymeric skeletons with pendant acid groups, such as phosphoric, phosphonic, sulfuric or sulfonic, chemically bonded thereto. The "exchange potential" of the chemically

bonded acid groups and the number of such groups available for contact with the "phenol" mixture indicates the effectiveness of a particular ion-exchange resin. Thus, although the number of acid groups chemically bonded to the polymeric skeleton of the resin determines the theoretical "exchange capacity" thereof, a more accurate criterion of effectiveness is the number of acid groups which are in fact available for contact with the reactants. This contact can occur on both the interior and exterior surfaces of the ion-exchange resin. As a general rule, therefore, a form of ion-exchange resin which provides a maximum amount of surface area, e.g., porous microspheres or beads, is highly desirable.

60 In general, the greater the "exchange capacity" of an ion-exchange resin, i.e., the greater the number of milli-equivalents of acid per gram of dry resin, the more desirable the resin for purposes of this invention. Resins having an "exchange capacity" greater than about two milli-equivalents of acid per gram of dry resin are preferred. Among the ion-exchange resins which are highly desirable are: sulfonated styrene divinylbenzene resins, sulfonated cross-linked styrene resins, phenol-formaldehyde-sulfonic acid resins, benzene-formaldehyde-sulfonic acid resins and the like. These and other such resins are available commercially under trade names such as: Amberlite XE-100 (Rohm and Haas Co. "Amberlite" is a registered Trade Mark), Dowex 50-X-4 (Dow Chemical Co. "Dowex" is a registered Trade Mark), Permutit OH (Permutit Co. "Permutit" is a registered Trade Mark), Chempro C-20 (Chemical Process Co.) and Amberlyst 15 (Rohm and Haas Co. "Amberlyst" is a registered Trade Mark).

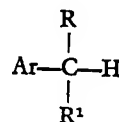
Other suitable cation exchange resins are described in British Patent 1,108,584.

Particularly preferred for purposes of this invention are ion-exchange resins, containing pendant sulfonic acid groups, which are saturated with the phenol to be treated.

As previously stated, a mixture of a phenol and carbonyl-containing impurities results from the cleavage of a hydroperoxide produced from the oxidation of an alkyl substituted aromatic hydrocarbon.

Suitable alkyl substituted, aromatic hydrocarbons, which can be oxidized to the corresponding hydroperoxides, can be represented by the following formula:

Formula I



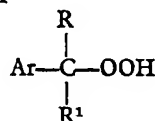
wherein Ar is an aryl radical generally having a maximum of fifteen carbon atoms and preferably having a maximum of ten carbon atoms and R and R¹, which can be the same or different, are alkyl radicals, each generally having a maximum of ten carbon atoms and each preferably having a maximum of five carbon atoms.

Specific compounds falling within the scope of Formula I are exemplified by: cumene, (isopropylbenzene), *p*-di-isopropylbenzene, *m*-di-isopropylbenzene, *p*-isopropyltoluene, secondary-butylbenzene, and isopropyl-naphthalene.

The oxidation of alkyl substituted, aromatic compounds to the corresponding hydroperoxides can be carried out by methods well known in the art, as for example, is disclosed in U.S. patent 2,577,768.

Oxidation of compounds falling within the scope of Formula I results in hydroperoxides having the formula:

Formula II



wherein Ar, R and R¹ are as previously defined.

Cleavage of the hydroperoxides produced by the oxidation of an alkyl substituted, aromatic hydrocarbon can be carried out by methods well known in the art, as for example, is disclosed in U.S. patent 2,626,281.

Separation of a mixture containing a phenol and carbonyl-containing impurities, from the other constituents of the mixture resulting from the cleavage reaction can also be carried out by methods well known in the art, as for example by fractional distillation as disclosed in U.S. patent 2,910,511.

Contact between the mixture containing a phenol and carbonyl-containing impurities and the ion-exchange resins can be effected in a batch operation wherein the mixture and the ion-exchange resin are brought together in a suitable vessel; or in a continuous operation wherein the mixture is continuously passed through a bed of the ion-exchange resin.

The temperature of the mixture containing a phenol and carbonyl-containing impurities, during contact with the ion-exchange resin, is not critical and can vary over a wide range, from the freezing point of the phenol to the degradation point of the ion-exchange resin. As a general rule, the temperature ranges from 50°C. to 185°C., preferably 50°C. to 130°C. The mixture if desired, can be pre-heated, can be heated while in contact with

the ion-exchange resin or the ion-exchange resin itself can be pre-heated.

Also, the time of contact between the mixture and the ion-exchange resin is not critical. The time of contact is sufficient to convert carbonyl-containing impurities to compounds having boiling points higher than the boiling point of the phenol. The actual time of contact will depend upon a number of factors including the exchange capacity of the ion-exchange resin, the amount of ion-exchange resin being used as well as the amount of mixture being treated. From a practical standpoint, the contact time involving a batch operation ranges from a few minutes duration, i.e. about 15 minutes, to about one hour. Greater contact times can be employed if the need arises.

Separation of the phenol from the insoluble ion-exchange resin can be effected by a simple filtration operation.

In the examples which follow, the ion-exchange resin used, Amberlyst 15, a styrene-divinylbenzene copolymer, having pendant sulfonic acid groups, was saturated with dry phenol by being washed with dry phenol until the phenol washings had a freeze point of >40°C.

Also, the *Phenol Purity Test*—which indicates the presence or absence of carbonyl-containing impurities was conducted as follows:

Twenty grams of the phenol, to be tested, and 0.2 gram of *p*-toluene sulfonic acid were placed in a 100 ml. beaker and the beaker placed on a hot plate. The contents of the beaker were brought to a temperature of 100°C. and maintained at this temperature for 30 minutes. At the end of the 30 minute period, the beaker was removed from the hot plate and the contents thereof poured into a beaker containing an equal weight portion of concentrated ammonium hydroxide. The color of the resultant solution was noted and rated as follows:

A colorless solution is indicative of a high purity phenol suitable for use in the production of high quality Bisphenol-A.

A reddish-violet colored solution is indicative of poor quality phenol which is unacceptable for use in the production of Bisphenol-A.

Example I

Three thousand four hundred grams of phenol product, produced by oxidizing cumene and cleaving the resultant hydroperoxide as described in the patents previously noted, were placed in a 5 liter flask which also contained 360 grams of Amberlyst 15. The resultant mixture was heated at a temperature of 125°C. for 2 hours while being mildly agitated. At the end of the 2 hour period, a 2588 gram portion of the treated phenol was filtered into a flask and batch distilled through

a 10 plate Oldershaw column under the following conditions:

5 pressure =72 mm Hg
 reflux ratio =2:1
 vapor temperature =112°C.

10 Two thousand four hundred and ten grams of phenol were recovered as a distillate (an overhead). One hundred and seventy-eight grams of material remained in the distillation flask.

 Analysis of phenol, by gas chromatography, before and after purification showed a 10 fold reduction in low boiling impurities.

15 Gas chromatography analysis results are tabulated below.

	Feed Phenol (ppm)	Purified Phenol (ppm)
20 Acetone	11	1
Mesityl oxide	76	1
Cumene	23	1
Acetol		
(hydroxyacetone)	218	9
25 α -Methylstyrene	—	19
3-Methylbenzofuran	17	9
Acetophenone	84	—
Unknowns	49	—
Total	478	40

30 The purified phenol produced a colorless solution when subjected to the Phenol Purity Test.

 The feed phenol (not purified) produced a reddish-violet solution when subjected to the Phenol Purity Test.

35 The water content of the phenol product of this example was 0.07 percent by weight, based on the total weight of the mixture. Water content as noted in this specification

was determined by the Freezing Point Depression test and by the Karl-Fischer method.

Example II

Phenol, produced as described in Example I was brought into contact with Amberlyst 15 in a continuous process wherein the phenol, which was at a temperature of 100°C. was passed through a bed of 0.1 cu. ft.³ Amberlyst 15 at the rate of 3 lbs. per hour.

The purified phenol was then recovered by a distillation operation as described in Example I.

The purified phenol produced a colorless solution when subjected to the Phenol Purity Test.

In order to further establish the necessity of treating a substantially anhydrous "phenol," i.e. containing a maximum of about 2.5 percent by weight water, (based on the total weight of the mixture—combined weight of water and phenol product) in accordance with this invention, water in various amounts was added to samples of phenol, produced as described in Example I. After the water addition, 800 gram samples were placed in a flask containing 80 grams of Amberlyst 15 and the resultant mixtures heated at a temperature of 100°C. for 2 hours. At the end of the 2 hour period, the phenol samples were removed from the ion-exchange resin by filtration and distilled in a manner described in Example I to recover dry phenol fractions.

"Phenols" were then analysed for carbonyl-containing impurities by testing for mesityl oxide content, a key carbonyl-containing impurity. The results are set forth in the table below. In this table, untreated phenol, refers to phenol which was not contacted with an ion-exchange resin but which was distilled as described in Example I.

The water content of the phenol product before ion-exchange treatment was 0.07 percent by weight.

SAMPLES

	A	B	C	1	2	Controls 3	4	5*
85 Percent by weight water added	0	2	2.5	5	10	15	20	0
Mesityl oxide content ppm	0	0	0	30	55	93	101	107

90 *Untreated

Samples, A, B, and C produced colorless solutions when subjected to the Phenol Purity Test.

95 Samples, Controls 1—5 produced reddish-violet solutions when subjected to the Phenol Purity Test.

 Example 1 was repeated with comparable results using "phenol" recovered from the

- 1—secondary-butylbenzene
 2—*p*-isopropyltoluene
 3—*m-di*-isopropylbenzene
 4—*p-di*-isopropylbenzene

Removal of water from a phenol product to a maximum level of about 2.5 percent by weight can be accomplished by extractive distillation in the presence of monochlorobenzene.

- 5 The abbreviation, ppm, means parts per million in terms of weight.

WHAT WE CLAIM IS:—

1. A process for the purification and recovery of a phenol from a substantially anhydrous mixture, containing said phenol and carbonyl-containing impurities which comprises contacting said mixture with a solid acidic ion-exchange resin which is insoluble in said mixture and which has pendant acid groups chemically bonded thereto to convert carbonyl-containing impurities to products having boiling points higher than the boiling point of said phenol and distilling the phenol therefrom.

- 20 2. A process as claimed in claim 1 wherein said pendant acid groups are phosphoric, phosphonic or sulfuric acid groups.

3. A process as claimed in claim 1 or 2 wherein the ion-exchange resin has pendant sulfonic acid groups chemically bonded thereto.

4. A process as claimed in any one of the preceding claims wherein said resin is a sulfonated styrene-divinylbenzene resin, sulfonated cross-linked styrene resin, a phenol-formaldehyde-sulfonic acid resin or a benzene-formaldehyde-sulfonic acid resin.

5. A process as claimed in claim 3 or 4 wherein said resin, containing pendant sulfonic groups, is saturated with the phenol to be treated.

6. A process as claimed in any one of the preceding claims wherein the temperature of said anhydrous mixture while in contact with the ion-exchange resin is 50°C. to 185°C.

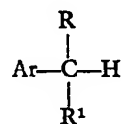
7. A process as claimed in any one of the preceding claims wherein the temperature of said anhydrous mixture while in contact with the ion-exchange resin is 50°C. to 130°C.

8. A process as claimed in any one of the

preceding claims wherein the anhydrous mixture is passed as a continuous stream through a bed of said acidic, ion-exchange resin.

9. A process as claimed in any one of the preceding claims wherein said substantially anhydrous mixture results from the cleavage of a hydroperoxide produced from the oxidation of an alkyl substituted, aromatic hydrocarbon.

10. A process as claimed in claim 9 wherein the alkyl substituted, aromatic hydrocarbon has the formula:



wherein Ar is an aryl radical having a maximum of 15 carbon atoms and R and R¹ are alkyl radicals which can be the same or different having a maximum of 10 carbon atoms each.

11. A process as claimed in claim 10 wherein said aryl radical has a maximum of 10 carbon atoms.

12. A process as claimed in claim 10 or 11 wherein said alkyl radicals R and R¹ each have a maximum of 5 carbon atoms.

13. A process as claimed in any one of claims 10 to 12 wherein said alkyl substituted hydrocarbon is cumene, *p*-di-isopropylbenzene, *m*-di-isopropylbenzene, secondary-butylbenzene or isopropylnaphthalene.

14. A process as claimed in claim 1 substantially as hereinbefore described with reference to and as illustrated in any one of the foregoing examples.

15. A phenol whenever produced by a process as claimed in any one of the preceding claims.

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